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Lubrication

A Technical Publication Devoted to
the Selection and Use of Lubricants

THIS ISSUE

Analytical Physics in the
Petroleum Industry

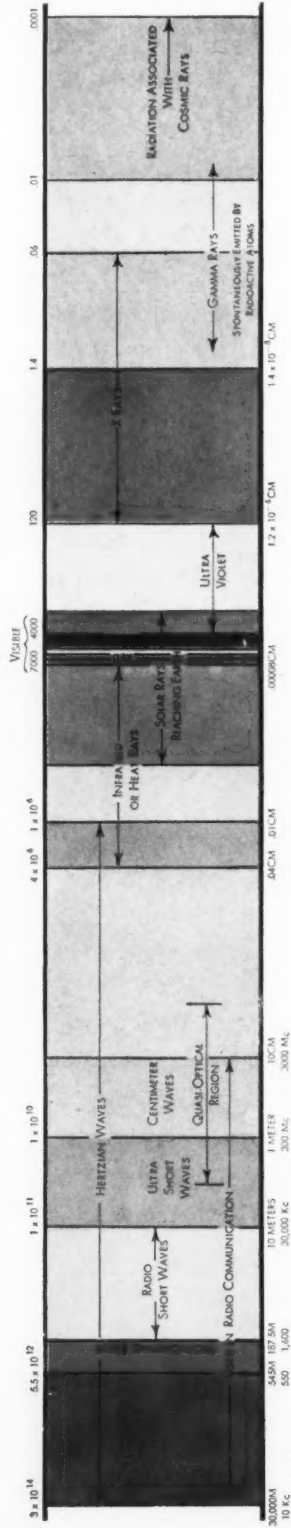


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THE TEXAS COMPANY
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ANGSTROM UNITS

(1 Angstrom Unit = 10 Millimicrons = 10^{-8} CM)



THE TOOLS OF RESEARCH

MASS PRODUCTION led to the perfection of the tools of industry. From the massive metal press to the finest precision machinery, they became essential to the manufacture of consumer goods before the war and even more vitally needed when high-speed war production was required.

But the tools of research, what of them? Most of us have visited some form of manufacturing plant and are familiar with the workings of the

planer, lathe, grinder, etc., or on outdoor work we can understand the operation of a riveter or power shovel.

The tools of research are naturally more delicate than these heavy-duty industrial machines; yet they are no more complex, and studied intelligently, their workings are generally as easy to visualize as the workings of a power shovel.

THE TEXAS COMPANY

LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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Analytical Physics in the Petroleum Industry

RESEARCH is commonly understood to require a variety of intricate apparatus. It does. Much of this apparatus, however, is not so formidable in its comprehension as its appearance would indicate. This is true of certain of the more modern types of petroleum research apparatus which are designed to employ well-known laws of physics. By applying the laws governing light (radiation) and the electrical properties of matter, for example, to the analysis of petroleum hydrocarbons, our ability to control the amounts and kind of components involved in the processes of refining has been definitely expanded.

As the laws of physics were applied to petroleum research, most interesting results were indicated. By varying pressure and temperature the research worker proved years ago that he could break up and fractionate a crude oil into those many valuable fuel and lubricating components which have come to be accepted as necessities in transportation and mass production.

By use of the absorption of radiation and of electronics he progressed much further. This ability to study petroleum hydrocarbons from a physical point of view contributed markedly to the perfection of high-octane aviation gasoline, synthetic toluene for explosives and synthetic rubber.

IMPORTANT PHYSICAL ANALYTICAL METHODS

Analyses of mixture of petroleum products are usually made by use of both physical and chemical methods. The physical properties on which analyses are ordinarily based include boiling point, freezing point, and index of refraction. The most widely used physical method of analysis is fractional dis-

tillation, which applies to materials having sufficiently different boiling points. When chemical methods are used to analyze for those components which cannot be separated by fractional distillation, accurate analyses of mixtures of all hydrocarbons having up to four carbon atoms (C_4), and a few C_5 's as well, are possible. Unfortunately, the time required for such analyses is seldom less than 24 hours.

In the search for more rapid analytical methods, other physical properties of hydrocarbons were studied. These include absorption of light or radiation in the ultraviolet and infrared spectral regions; the scattering of light, with change of wave-length, at right angles to the incident beam (Raman scattering); and the relative quantities of charged molecular fragments having different masses which are produced when a hydrocarbon is bombarded by an electron beam (mass spectroscopy). As a result, analytical methods based on the physical properties listed above have been developed which are very much more rapid than those previously used, and which permit the accurate analysis of many hydrocarbon mixtures which could not be analyzed satisfactorily by the older methods. The most important of these new methods, namely, infrared absorption spectroscopy and mass spectroscopy, will be discussed.

INFRARED ABSORPTION SPECTROSCOPY*

Infrared absorption spectroscopy is of particular value in the analysis of hydrocarbon mixtures and in the study of petroleum products generally because every organic molecule absorbs energy selectively in the infrared region of the electromagnetic spectrum.

*A more detailed discussion will be found in Barnes, Liddell, and Williams, *Ind. Eng. Chem. Anal. Ed.* 15, 659-709, 1943.

Very few materials of interest to the petroleum industry absorb energy in the visible spectral region, while in the ultraviolet region only olefins and aromatic compounds absorb. The most useful part of the infrared region of the electromagnetic spectrum extends between the wavelengths 1.5 microns and 25 microns (one micron = 10^{-4} cm.). It will be recalled that visible light has wavelengths between 0.4 and 0.7 microns, while the ultraviolet region lies between 0.2 and 0.4 microns.

Why Organic Molecules Absorb Infrared Radiation

That all organic molecules should absorb energy in the infrared region follows naturally from the way in which atoms are bound together to form a molecule. A molecule may be pictured as composed of masses (representing the atoms) which are held together by springs (representing the binding forces between the atoms). The molecule vibrates like such a mechanical system, and so has certain characteristic vibrational frequencies which are determined by its spatial structure, by the masses of the atoms, and by the binding forces between them. Radiation, (visible, infrared, radio, etc.) is recognized to be of a vibrating nature, whose frequency f is related to the wavelength λ , through the equation

$$f = \frac{c}{\lambda},$$

where c is the velocity of light. If radiation of a frequency equal to any one of the characteristic frequencies of a specific molecule falls upon that molecule, it interacts electrically with the molecule and causes it to vibrate at this frequency*, thus absorbing energy from the radiation. The characteristic frequencies of most organic molecules are such that the corresponding wavelengths lie in the useful infrared region.

What an Infrared Spectrograph Does

The incident radiation is produced by a glowing solid, such as a silicon carbide rod or a Nernst glower**, and has its radiant energy distributed in wavelength as shown schematically by Figure 1A. After this radiation has passed through a collection of absorbing molecules, its distribution with wavelength might look like that shown in Figure 1B, in which the result of absorption at specific wavelengths is pictured. The main instrumental problems of infrared absorption spectroscopy are to determine the wavelengths at which the absorptions shown on Figure 1B occur, and to measure their magnitude quantitatively. The resulting absorption

*Neglecting the effect of zero point energy.

**A thin rod made of oxides of cerium, thorium, and zirconium.

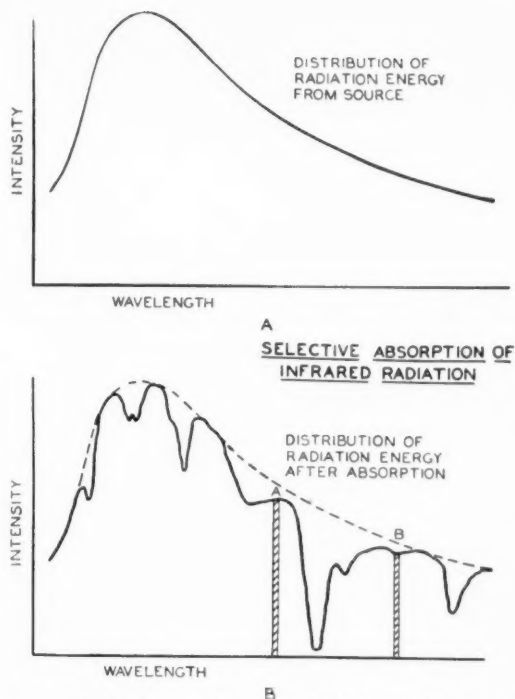


Fig. 1—(A) Variation with wavelength of the radiation intensity emitted by an infrared source. (B) Source radiation intensity after passing through test sample, showing selective absorption.

spectrum, in which the percentage of the incident radiation which is transmitted through the sample is plotted against the wavelength, is characteristic of the absorbing molecule and may be used to identify it.

How an Infrared Spectrograph Works

These two problems are solved by means of a spectrograph. The basic element of this instrument is the means of dispersing the radiation, that is, of separating the radiation having one wavelength from that having another. One simple means of doing this is the prism, which has two functions: (1) its geometry causes radiation passing through it to be bent through an angle which depends upon its index of refraction; and (2) its index of refraction varies with the wavelength of the radiation in such a way that rays of short wavelength are bent more than rays of long wavelength, as shown by Figure 2. Figure 3 shows all the elements of a simple spectrograph. The combination of the prism and the lenses forms a series of overlapping images of the entrance slit in the plane of the exit slit. Each of these images is produced by radiation having a different wavelength, due to the dispersing action of the prism. For example, in a typical infrared spectrograph the position of the image formed by radiation having a wavelength of 1.5 microns is approximately 40 centimeters distant from that of

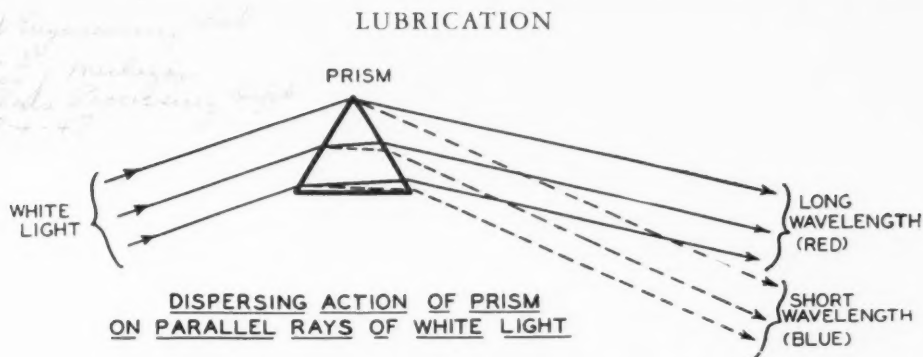


Fig. 2—Dispersing action of a prism. Due to its geometry and the variation of its index of refraction with wavelength, it bends the short wavelengths through a greater angle.

the image formed by radiation having a wavelength of 15 microns.

Only a narrow band of wavelengths from this spectrum passes through the exit slit and falls upon a thermocouple whose voltage output is proportional to the total radiation energy in this band. The measurement of this voltage gives the transmitted intensity, as at A on Figure 1B. Another position, such as B, can be measured by rotating the prism so that the narrow band passing through the exit slit is centered at another wavelength. If the prism is rotated continuously while the intensity of the radiation passing through the exit slit is being measured, a record on which intensity is plotted as a function of wavelength can be produced by means of a suitable recorder. If the unabsorbed radiation intensity is kept constant by varying the slit widths automatically, this record is the desired absorption spectrum of the sample being studied.

In the infrared region one can not use lenses because their focal length varies greatly with the wavelength. It is therefore necessary to replace the lenses by mirrors whose front surfaces are reflecting. All windows and prisms must be transparent to the infrared radiation. Windows of KBr (potassium bromide) are satisfactory over the entire region from 1.5 to 25 microns, while two prisms are used, one of NaCl (sodium chloride) for the region from 1.5 to 15 microns because of its greater dispersion, and one of KBr for the region between 14 and 25

microns because NaCl does not transmit in this region.

The Texas Company's Research Infrared Spectrograph

Figure 4 shows the optical arrangement of The Texas Company's research type of infrared spectrograph. The entire unit containing the Nernst glow radiation source, the spherical mirror, and the absorption cell can be moved laterally so that the radiation enters either the foreprism slit, as shown on the figure, or the prism slit at its left. After entering the prism slit, the radiation takes the path indicated. The optical arrangement is equivalent to that shown on Figure 3, the one off-axis paraboloidal mirror taking the place of the two lenses. The table holding the prisms is rotated by a worm and worm wheel.

Two gratings are also mounted on the rotating table. A grating is another kind of dispersing device which bends the rays through different angles according to their wavelength. It gives the increased resolution, that is, the increased ability to separate two absorbing regions which are close together in wavelength, which is required for certain analytical problems. When one of the gratings is being used the radiation enters the foreprism entrance slit and goes through a small foreprism spectrograph whose optical elements duplicate on a smaller scale those

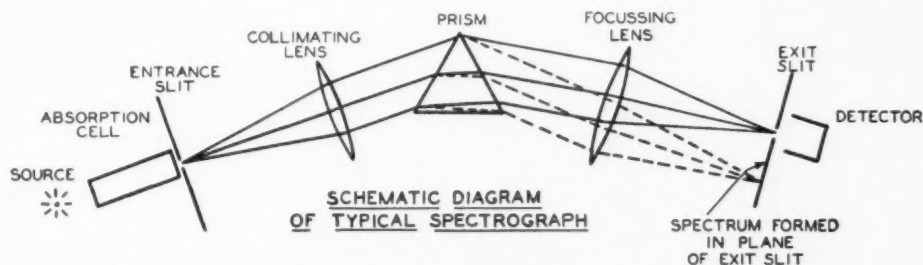


Fig. 3—A simple spectrograph. The radiation through the entrance slit is made parallel by the collimating lens, dispersed by the prism, and focussed on the exit slit plane by the focussing lens. Each image of the entrance slit so formed is due to a single wavelength of the incident radiation. The exit slit passes only a narrow band of wavelengths, whose intensity is measured by the detector.

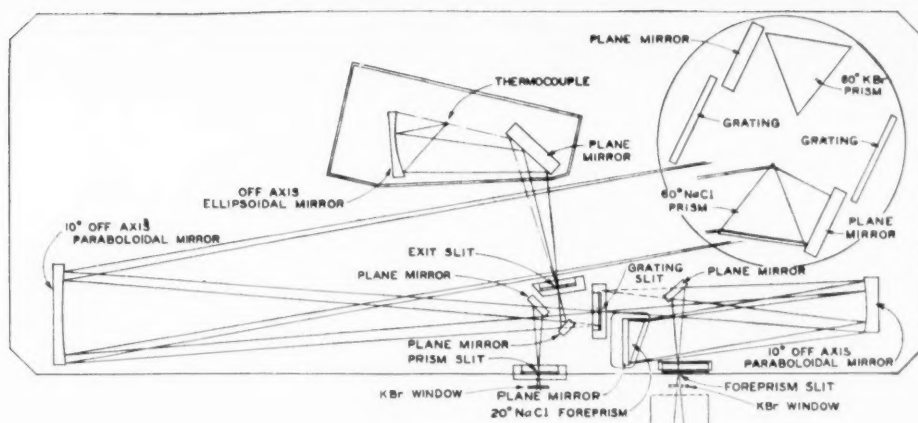


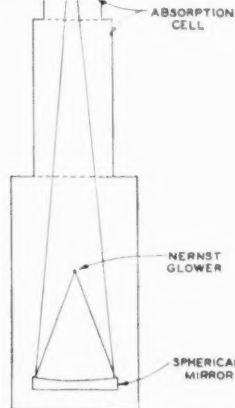
Fig. 4—Schematic diagram of the optics of The Texas Company's research type of infrared spectrograph and source housing.

in the large prism spectrograph. The dispersive characteristics of the grating require the use of the filtering action of this foreprism spectrograph.

Autosyns Used to Transmit Controlled Motion through Vacuum Tight Covers

Figure 5 shows a general photograph of the spectrograph. The heavy steel case, inside which the optical elements are mounted, is evacuated to remove completely all disturbing absorption by water vapor. The unit containing the oxide rod used as a source, as well as the absorption cells, is in the right foreground. The two units in the left foreground contain the electronic and mechanical controls necessary for producing the desired motion of the moving elements of the spectrograph. No motion is transmitted mechanically into the evacuated space. Instead, all motions inside the spectrograph case are produced either by induction motors operated by switches in the control unit or by two pairs of Autosyn motors. One Autosyn of each pair is located inside the case, the other being in the control unit. These Autosyns permit motion determined by cams located in the control unit to be accurately repeated in the spectrograph, so that automatic control of slit widths to give a constant thermocouple output with no absorbing sample in position, and automatic control of prism table angular velocity to give a linear wavelength scale, is possible. All motions are monitored by means of revolution counters.

Figure 6 shows a photograph with the spectrograph cover removed and the control unit absent. The prisms and gratings are visible on their table at the right. The black box in the center houses the thermocouple and its optical system, while the various slits are visible in the center foreground. The various driving mechanisms are located at the left.



Use of Electronic Amplification and Rapid Response Thermocouple Reduces Recording Time

The radiation entering the spectrograph is interrupted by rotating the two-lobed shutter visible in Figures 5 and 6 between the source unit and the entrance slit. In this way an alternating component is produced in the output of the thermocouple used to measure the radiation passing through the exit slit. A special vacuum tube amplifier is used to amplify the very small output voltage of the thermocouple. The amplifier output is recorded photographically by means of a rugged galvanometer.

The use of electronic amplification of the thermocouple output is a new development made possible by the construction of a new type of thermocouple whose temperature and output voltage accurately follow rapid changes in radiation intensity. Such thermocouples are made by condensing metal films three millionths of an inch thick on a resin supporting film only two millionths of an inch thick. The associated vacuum tube amplifier is capable of detecting an input voltage of less than 5.10^{-10} volt, that is, less than $1/2$ billionth of a volt.

This new method of detecting the infrared radiation makes possible an important reduction in the recording time, and a great increase in the overall stability of the radiation intensity measurement. It eliminates vibrational difficulties with sensitive galvanometers which have in the past required special mountings usually possible only in a research laboratory.

Figure 7 shows a typical absorption spectrum obtained with this spectrograph. The vertical lines are wavelength calibration marks.

The spectrograph which has been described is an expensive and versatile research instrument having high resolving power. The absorption spectra of pure hydrocarbon compounds which are obtained with it are the data on which the actual routine analytical methods are based. These routine analyses are carried out with a smaller and cheaper commercial spectrograph having a much lower resolving power.

Qualitative Analysis

The infrared absorption method has both qualitative and quantitative applications in the petroleum industry.

Both are based on the fact that the absorption spectrum of a given compound is an unique fingerprint which can not be duplicated by any other compound. An important qualitative application makes use of the empirical observation that certain atomic groups within a molecule have characteristic absorption wavelengths which are influenced only slightly by the remainder of the molecule. Typical examples* of such groups include:

1. Stretching of C—H bond, 3.2-3.4 microns
2. Stretching of C—C single bond, 8-12 microns
3. Stretching of C=C double bond, 6-6.2 microns
4. Stretching of C≡C triple bond, about 4.5 microns
5. Stretching of C=O double bond, about 5.8 microns
6. Stretching of O—H bond, 2.7-2.9 microns
7. Bending of H—C—H bond angle, 6.5-7.5 microns.

*R. R. Brattain, *Petroleum World*, February 1943.

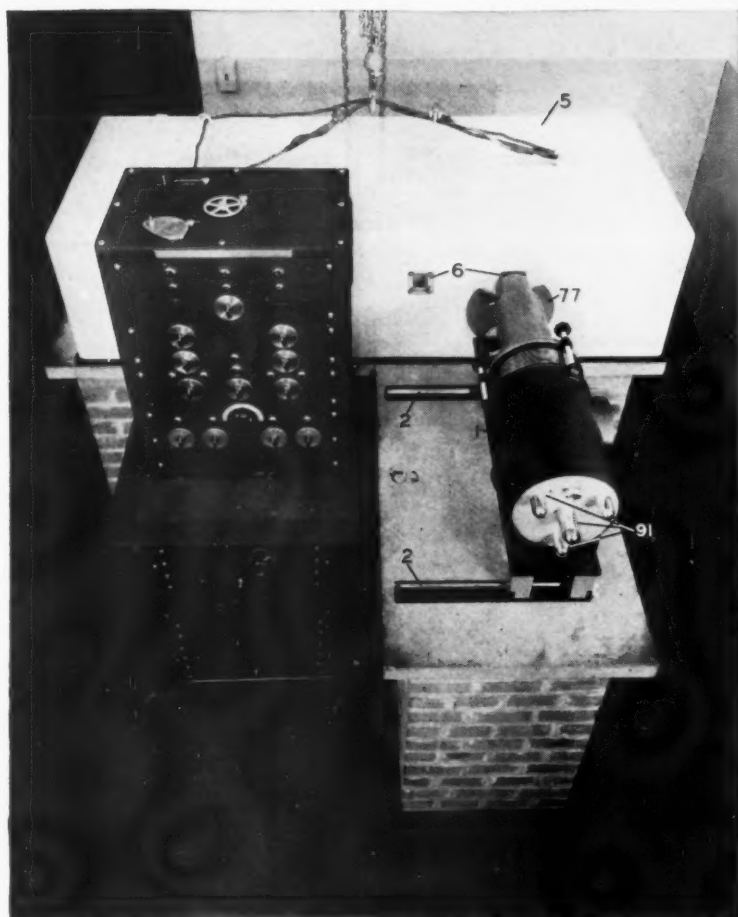


Fig. 5—General view of The Texas Company's research infrared spectrograph. The heavy steel case contains the optical elements, the source and absorption cells are in the right, while the electronic and mechanical controls are located in the racks at the left. The steel case is evacuated to remove disturbing absorptions due to water vapor.

In studying complex mixtures the identification of the presence of such groups is often of great value.

Types of Samples

An absorbing material can be examined in the vapor, liquid, or solid phase. For analytical work the vapor phase permits a higher accuracy, chiefly because the absorption cell length for liquids or the sample thickness for solids must be 0.1 mm. or less, and is difficult to reproduce. A sample having a liquid volume of 1 ml. is sufficient. Because liquid water or water vapor attack the NaCl or KBr windows, samples containing more than minute traces of H₂O cannot be handled. Because no solvent exists which does not absorb in the infrared region, solutions are difficult to study except in limited wavelength regions. CCl₄, carbon tetrachloride, and CS₂, carbon disulfide, are the most suitable solvents.

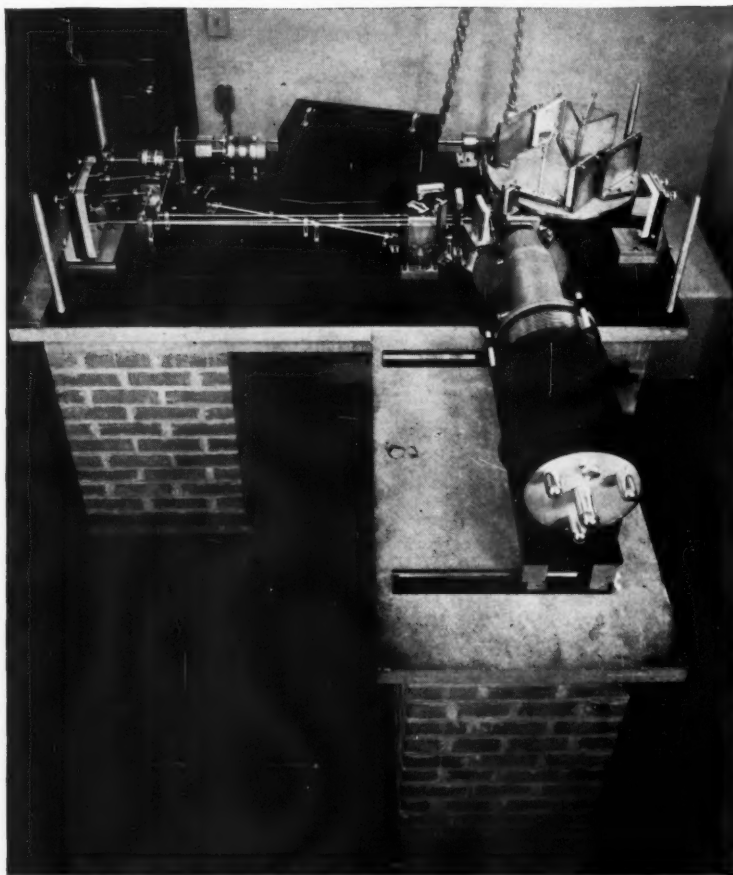


Fig. 6—The optical elements of The Texas Company's research infrared spectrograph. The prisms and gratings are located on the rotatable table at the right, the black box in the center houses the thermocouple and its optical system, while the four slits are visible in the center foreground. The electrical motors and Autosyns are located at the left.

Quantitative Analysis

All quantitative analysis require a previous calibration of the spectrograph with pure samples of all of the compounds for which an analysis is to be made. Because of differences in the resolving power and the amount of stray radiation from spectrograph to spectrograph, it is not possible to use an absorption spectrum determined on one spectrograph as a quantitative reference standard for analytical work with another.

The analytical method depends upon the finding of an absorption maximum for each compound in the mixture at a wavelength at which the other compounds absorb only slightly. From the calibration with the pure compounds and measurements on the unknown mixture, the data for a set of simultaneous equations are obtained, and the solution of these equations leads to the composition of the unknown sample. Such an analysis depends upon the assumption that molecular interaction be-

tween the various compounds of the mixture is not serious, since otherwise the absorption spectrum of the mixture would not be simply related* to the spectra of its individual components.

Figure 8 shows the absorption spectra of four octanes commonly present in alkylates. The dotted lines indicate typical key wavelengths of a mixture containing them.

Analytical Accuracy and Speed

At the present time quantitative analysis by infrared absorption of seven component mixtures of hydrocarbon gases is possible with an accuracy of about $\frac{1}{2}$ per cent. These gases include all the C_4 hydrocarbons which are of great importance in connection with the various processes mentioned in the Introduction. Such an analysis requires approximately one half to one hour, including the computing time. The analysis of multicomponent liquid samples, such as alkylates, can be carried out by separating the sample into narrow boiling cuts by fractional distillation, and then

analyzing each cut separately. Although the total time required may be three days, the resulting analysis could not be obtained without the use of infrared absorption or the mass spectrograph described below. It has the great advantage of telling exactly what materials the particular alkylation operating conditions produced, and its significance is independent of future changes in the more usual methods of evaluating alkylates, such as octane number.

*The optical density (the logarithm of the reciprocal of the per cent transmission) of a non-interacting mixture is the sum of the optical densities of its components.

MASS SPECTROMETER**

Like the infrared spectrograph, the mass spectrometer has been used in physical research for many years, but it is only in the last several years that its latent advantages as an analytical tool of great value to the petroleum industry have been ex-

**Washburn, Wiley, and Rock, *Ind. Eng. Chem. Anal.* Ed 15, 541-8, (1943).

ploited. It is particularly useful in the analysis of mixtures of hydrocarbon gases, that is, hydrocarbons having less than five carbon atoms, but its ability to handle hydrocarbons having up to eight or nine carbon atoms is rapidly being developed.

Even when consideration is restricted to the analysis of hydrocarbon gases, the problem is very complex. The 23 hydrocarbons having less than five carbon atoms are listed in Table I. The groups which low temperature fractional distillation does not readily separate are indicated by brackets. The members of these groups are ordinarily determined by chemical methods. Fortunately ten of these hydrocarbons are not commonly present, but often N_2 , O_2 , and H_2 are required in addition, so that it is not unusual for a mixture on which a routine analysis is desired to contain from 10 to 16 components.

TABLE I
HYDROCARBON GASES

	B.P., °C.
1. Methane CH_4	-161.4
2. Ethylene C_2H_4	-103.9
3. Ethane C_2H_6	-89.0
4. Acetylene C_2H_2	-83.6
5. Propane C_3H_8	-42.1
6. Propylene C_3H_6	-47.6
*7. Propadiene C_3H_4	-34.3
*8. Methylacetylene C_3H_4	-23.2
*9. Cyclopropane C_3H_6	-32.9
10. iso-Butane C_4H_{10}	-11.72
11. Butylene-1 C_4H_8	-6.24
12. Isobutylene C_4H_8	-6.67
13. 1, 3-Butadiene C_4H_6	-4.54
14. n-Butane C_4H_{10}	-0.5
15. cis-Butylene-2 C_4H_8	3.73
16. trans-Butylene-2 C_4H_8	0.96
*17. 1, 2-Butadiene C_4H_6	10.3
*18. Ethyl-acetylene C_4H_6	8.6
*19. Dimethyl-acetylene C_4H_6	27.1
*20. 1, 3-Butadiyne C_4H_2	10.3
*21. 3-Buten-1-yne C_4H_4	5.0
*22. Methyl cyclopropane C_4H_8	4.5
*23. Cyclobutane C_4H_8	13.08

*Not commonly found.

What a Mass Spectrograph Does

The mass spectrograph is basically an instrument for measuring the number of positive ions in a mixture which have the same charge to mass ratio. If

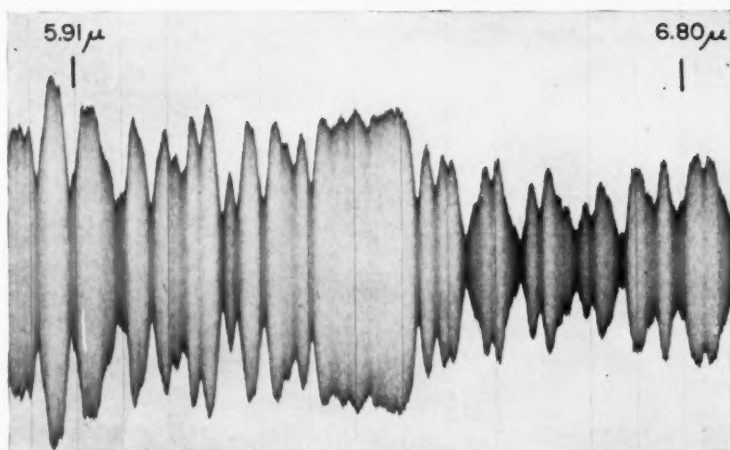
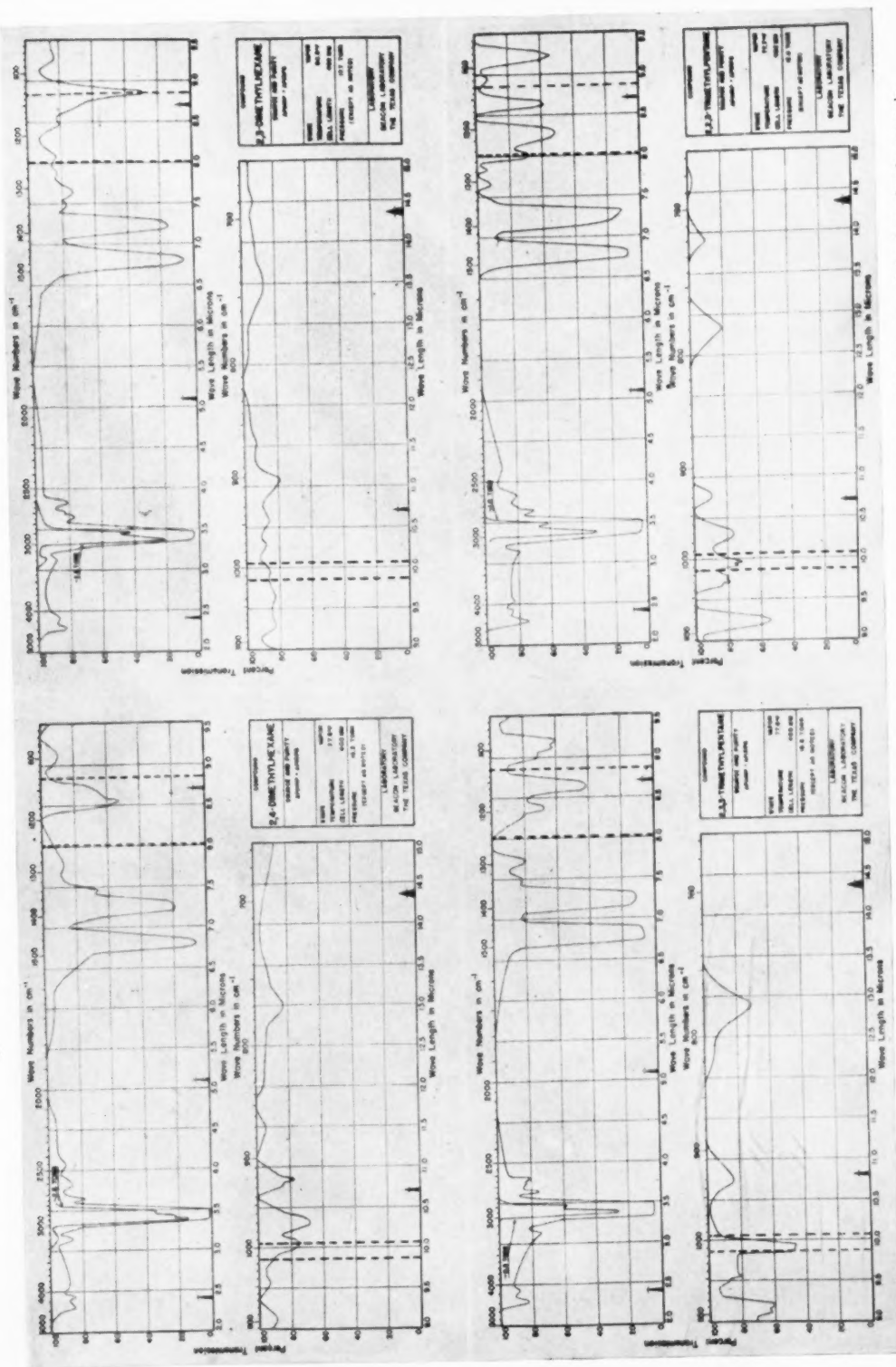


Fig. 7—Water vapor absorption spectrum obtained with the research spectrograph.

a mixture of hydrocarbon gases could be ionized by electron bombardment in such a way that from each parent molecule only its singly charged positive ion was formed, then those components of the mixture which differed in mass could be determined quantitatively at once in a very simple way, but isomers could not be separated. Practically it is not possible to ionize a mixture of hydrocarbons without breaking each parent molecule into positively charged fragments whose mass and relative abundance depend upon its chemical structure, that is, the strengths of the bonds between its atoms. Experiment shows that each pure hydrocarbon has an unique dissociation pattern or mass spectrum which expresses the relative abundance of the singly charged fragments as a function of their mass. Such a pattern for ethane is shown on Figure 9. These patterns are distinctly different for most isomers, but show only small differences for stereoisomers such as cis- and trans-2-butylene.

Under proper conditions the mass spectra of the individual components add linearly to form the mass spectrum of the hydrocarbon mixture. If the spectra of the pure components are known from previous calibration, then an unknown mixture can be analyzed as soon as its spectrum has been obtained. This analysis requires the solution of a set of simultaneous linear equations, theoretically of order equal to the number of components, but practically of much lower order.

With the mass spectrograph manufactured by The Consolidated Engineering Company, which is now being used by many petroleum companies, a 14 component mixture of hydrocarbon gases can be analyzed in two to three hours with an accuracy of about one per cent of the total mixture. The accuracy varies with the particular hydrocarbon, being poorer for the separation of 1- and 2-butylene, but is comparable with or better than that obtained in



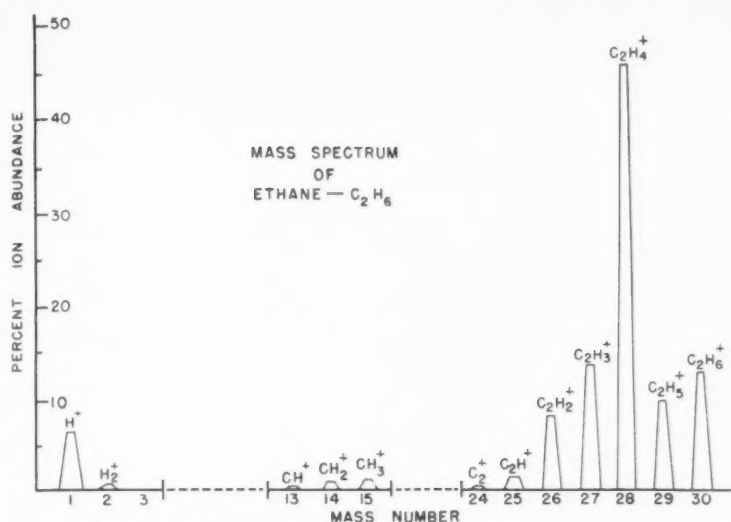


Fig. 9—Mass spectrum of ethane, showing per cent abundance of each ionic fragment. This pattern changes with mass spectrograph operating conditions, which must be constant to obtain accurate analysis.

routine work with the combination of low temperature fractional distillation and chemical methods mentioned above.

Types of Mass Spectrographs

The two main types of mass spectrographs are illustrated schematically in Figure 10. In the first type, (Figure 10A), of which The Consolidated Engineering Company's instrument is an example, the ion beam is completely immersed in a magnetic field from the time it is generated to the time it is measured. This field bends the beam through a complete semicircle. In the second type, (Figure 10B), the ion beam is deflected by a magnetic field having a limited extent, the angle θ usually being either 60° or 90° . A magnetic field is sometimes used in the ion source to focus the electron beam. The action of the mass spectrograph will be described in terms of the second type of construction.

How a Mass Spectrograph Works

On Figure 11 are shown schematically the important elements of any mass spectrograph. The sample to be analyzed is admitted through a tiny hole to a chamber in which the pressure is of the order of 10^{-4} mm. Hg. In this chamber a beam of electrons, emitted by a hot filament and accelerated by a potential of 70-100 volts, bombards the gas molecules, producing the positively charged ions mentioned above. These ions are then accelerated by an electric field produced by a potential difference of the order of 1000-3000 volts between two plates having slits in them, so that a ribbon-shaped ion beam is formed. This beam travels down the

center of the analyzer tube, in which the pressure is less than 10^{-6} mm. Hg., so that very few collisions with other molecules occur. A portion of the analyzer tube is immersed in a strong magnetic field whose lines of force are perpendicular to the beam direction. This field causes an individual ion in the beam to move in a circular path whose radius depends upon the ratio of the charge on the ion to its mass, and also upon the energy which the ion acquired during the acceleration process. Since this energy is the same for all ions, and since most of the ions have a single charge, a series of curved ion beams is formed whose curvature depends only upon the ionic mass, the

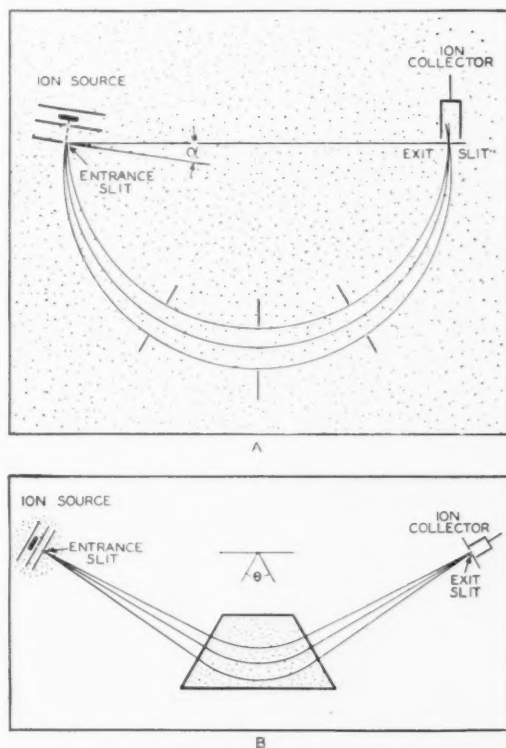


Fig. 10—(A) Dempster or 180 degree type of mass spectrograph. The ions are immersed in the magnetic field, shown by dots to indicate that it is perpendicular to the paper, from generation to measurement. (B) Nier type of mass spectrograph, using a magnetic field of limited extent. The magnetic field at the ion source is used to focus the electron beam.

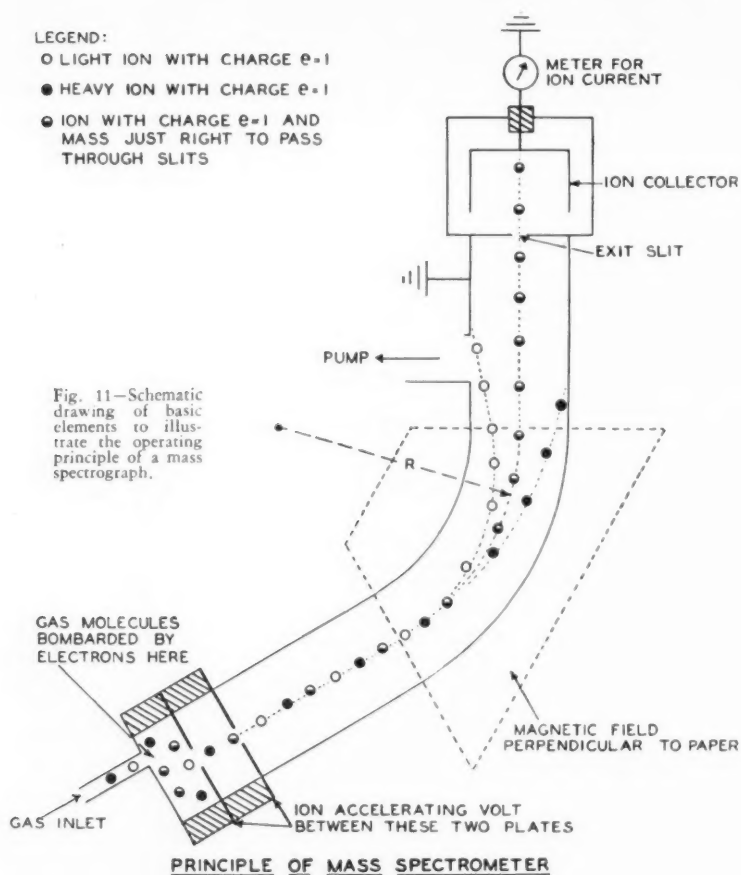


TABLE II
 ANALOGY BETWEEN RADIATION SPECTROGRAPH
 AND MASS SPECTROGRAPH

Light Spectrograph	Mass Spectrograph
Source	Source
Entrance Slit	Entrance Slit
— — —	Accelerating Electric Field
Collimating Lens	Magnetic Field
Prism	
Focusing Lens	
Exit Slit	Exit Slit
Photomultiplier	Faraday Cage + Electrometer Tube

Spectrum Varied By

- | | |
|-------------------------------------|---|
| a. Fixed Prism — Photographic Plate | a. Fixed Electric and Magnetic Fields — Photographic Plate |
| b. Fixed Prism — Moval Exit Slit | b. Fixed Fields — Movable Exit Slit |
| c. Rotating Prism — Fixed Exit Slit | c. Fixed Magnetic Field—Variable Electric Field—Fixed Exit Slit |
| | d. Fixed Fields—Several Exit Slits |

heavier ions being bent less and the lighter ions more. Proper adjustment of the acceleration voltage (the magnetic field strength is usually kept constant) enables the operator to bend those ions having a particular mass through just the right arc to make them pass through the exit slit into the ion collector. The current formed by the ions striking the ion collector is measured by a sensitive electronic method. The ions which do not go through the exit slit strike the metal lining of the analyzer tube or the metal plate in which the exit slit is located and their charges are neutralized. The beam intensity is so low that more than 20 days would be required for the formation of a monolayer of the discharged ions, assuming that all which strike a surface remain on it. The current measured by the ion collector is recorded automatically as the ion acceleration voltage is varied, and the mass spectrum mentioned above is obtained.

Analogy Between Mass Spectrograph and Light Spectrograph

The close analogy between the light or radiation spectrograph and the mass spectrograph is shown on Figure 12, while Table II lists the parts of each type of spectrograph which perform analogous functions. It will be noted that the magnetic field acts not only as a dispersing medium, but also provides the necessary focussing. It is therefore equivalent to the two lenses and the prism of the light spectrograph.

Figure 13 shows a typical mass spectrum of isobutane obtained on a mass spectrograph being developed by The Texas Company for use in research. Only the three

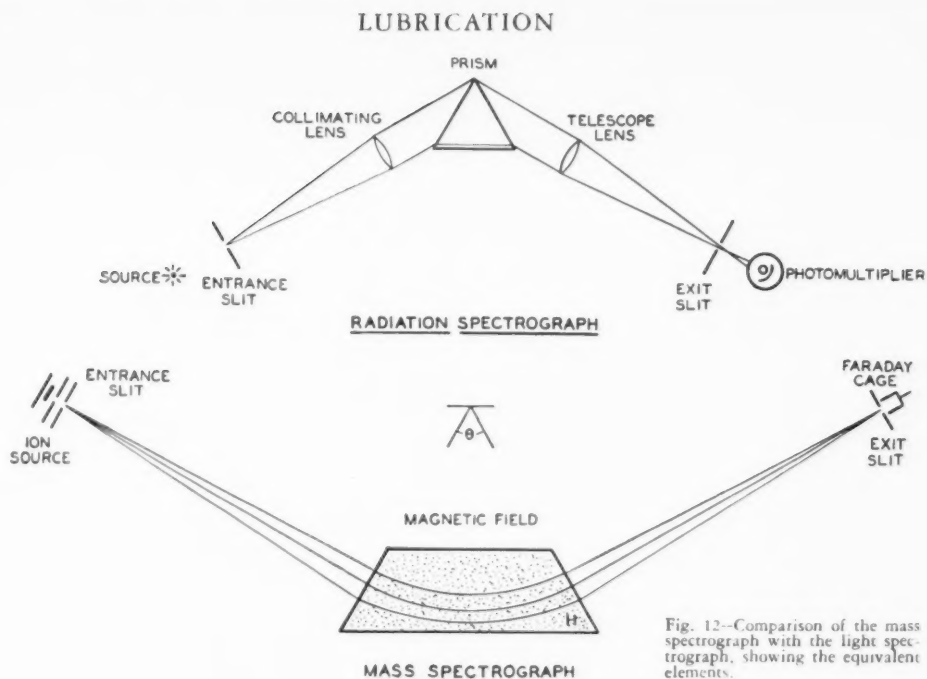


Fig. 12--Comparison of the mass spectrograph with the light spectrograph, showing the equivalent elements.

most useful portions of the mass scale are shown. The use of four recording galvanometers having sensitivities of 1, 1/3, 1/10, and 1/30, which was initiated by The Consolidated Engineering Company, makes possible accurate measurements of peaks having very different heights.

Figure 14 is a photograph of a mass spectrograph built by The Consolidated Engineering Company and installed in the Port Arthur Refinery of The Texas Company. At the extreme left is located the sample handling equipment, the spectrograph proper between the poles of the magnet is located in the corner, while the electronic controls and the recording system are located behind the panels at

the right.

Some typical mixtures which have been analyzed by The Consolidated Engineering Company's mass spectrograph are given in Table III, together with the overall time required per sample. Most of this time is taken by the computations, since only 40 to 45 minutes is required to run the sample and measure the record. Prorated calibration time varies from 10 minutes to 45 minutes depending upon the complexity of the sample. The total sample required is of the order of 0.1 ml. liquid. Samples can be run at the rate of about 20 per eight hour day, so that one instrument operator can keep three to four computers busy.

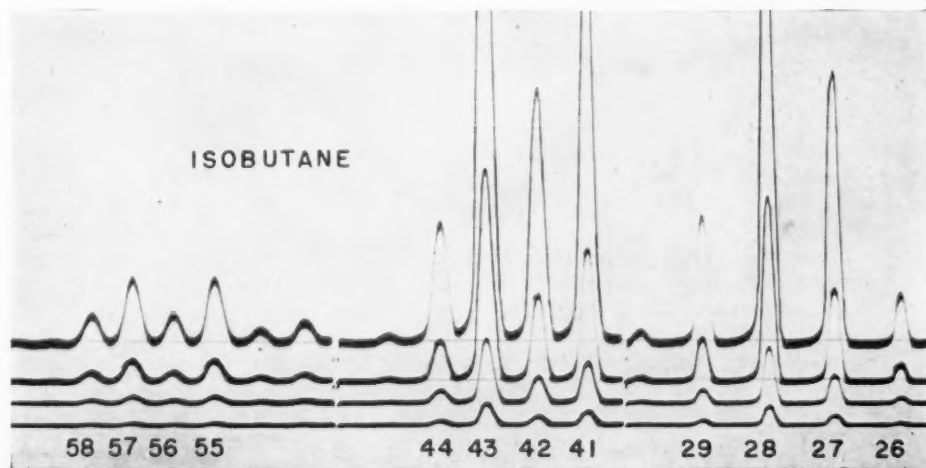


Fig. 13--Mass spectrum of isobutane obtained with The Texas Company's research mass spectrograph. The four traces are produced with recording galvanometers having sensitivities of 1, 1/3, 1/10, and 1/30.

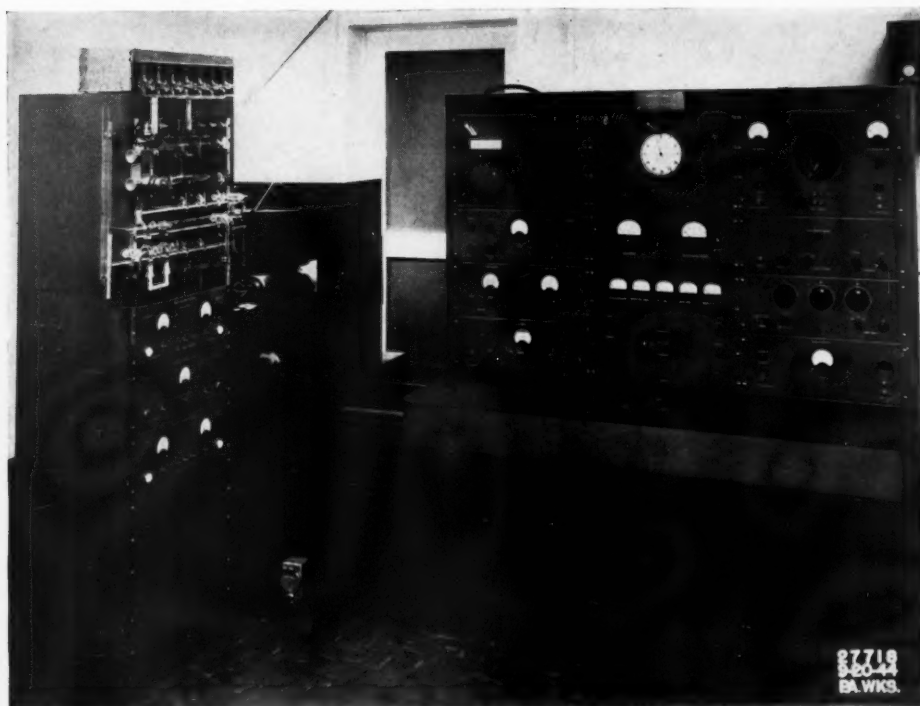


Fig. 14—Mass spectrograph built by The Consolidated Engineering Company and used by The Texas Company's Port Arthur Refinery for routine hydrocarbon gas analysis.

TABLE III
TYPICAL HYDROCARBON MIXTURES ANALYZED BY MASS SPECTROGRAPH

<i>Composition</i>	<i>No. of Components</i>	<i>Analysis Time-Hours</i>
Wet Gas	12	1.5
C ₁ through C ₄ paraffin and olefin	10	2.0
C ₃ through C ₅ paraffin and olefin	10	2.25
C ₄ paraffin, olefins, and diolefin	7	1.5
C ₅ paraffin, olefins, diolefins, and cyclic	6	3.8
C ₅ — C ₆ paraffins, cycles, and aromatics	9	4.25
Benzene, toluene, and xylenes in gasoline	4+	2.8

COMPARISON OF INFRARED SPECTROGRAPH AND MASS SPECTROGRAPH METHODS OF ANALYSIS

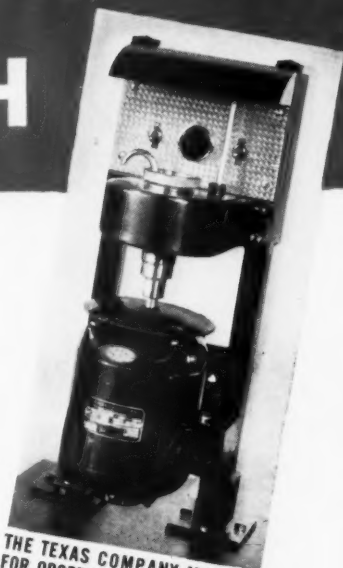
It can be seen from the preceding discussion that the infrared absorption spectrograph and the mass spectrograph are both analytical tools of great power. Each has its own sphere of application, and these spheres overlap considerably. The mass spectrograph method can analyze for O₂, N₂, and H₂, while the infrared method cannot, since these molecules do not absorb in the infrared. The mass spectrograph can analyze mixtures having more components than the infrared spectrograph because there are many more peak positions, all sharply defined, from which to choose, while difficulties due to lack of separation of absorption regions will limit the number of components for which the infrared method can analyze. With the mass spectrograph, the sample pressure in the ion source is so small that there is no interaction between the

various components, and the simultaneous equations to be solved are linear. With the infrared method, appreciable interaction between components in the sample, whether liquid or vapor, often causes departure from linear superposition, and this, together with the non-linearity caused by the use of wide slits on routine spectrographs, increases the complexity of the computations and the amount of calibration data required. The infrared method can be applied to solids and to low vapor pressure liquids which the mass spectrograph cannot handle. It can make qualitative identification of atomic groups, and separate stereoisomers accurately, neither of which the mass spectrograph can do in general. Both methods require a very small sample, but the infrared method does not alter it in any way, while it is lost in the mass spectrograph.

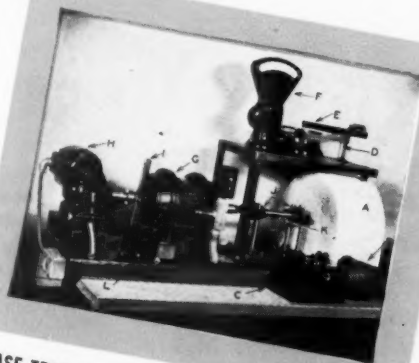
GREASE RESEARCH

PETROLEUM products undergo transitions like everything else. Petroleum greases have been especially "transitional." It is a "far cry" back to the conventional lime soap cup greases of the World War I Era. The grease chemists and the steel metallurgists have come a long way since then. They have learned a lot meanwhile. Outstanding among their developments have been the several precision instruments for testing grease and anti-friction bearing performance. Without them industry and transportation could never have had the precision ball bearing, the heavy-duty roller bearing and *Texaco Regal Starfaks*.

THE TEXAS COMPANY

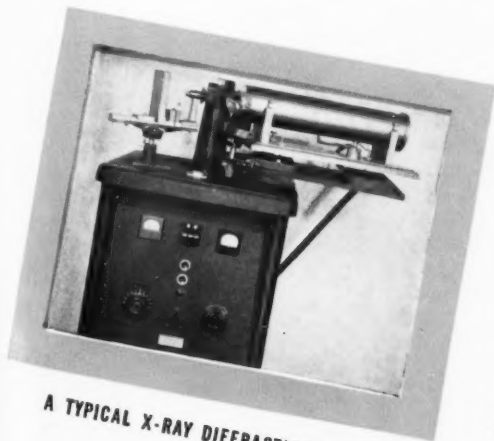


THE TEXAS COMPANY MACHINE
FOR OBSERVING GREASE PERFORMANCE
IN BALL BEARINGS.

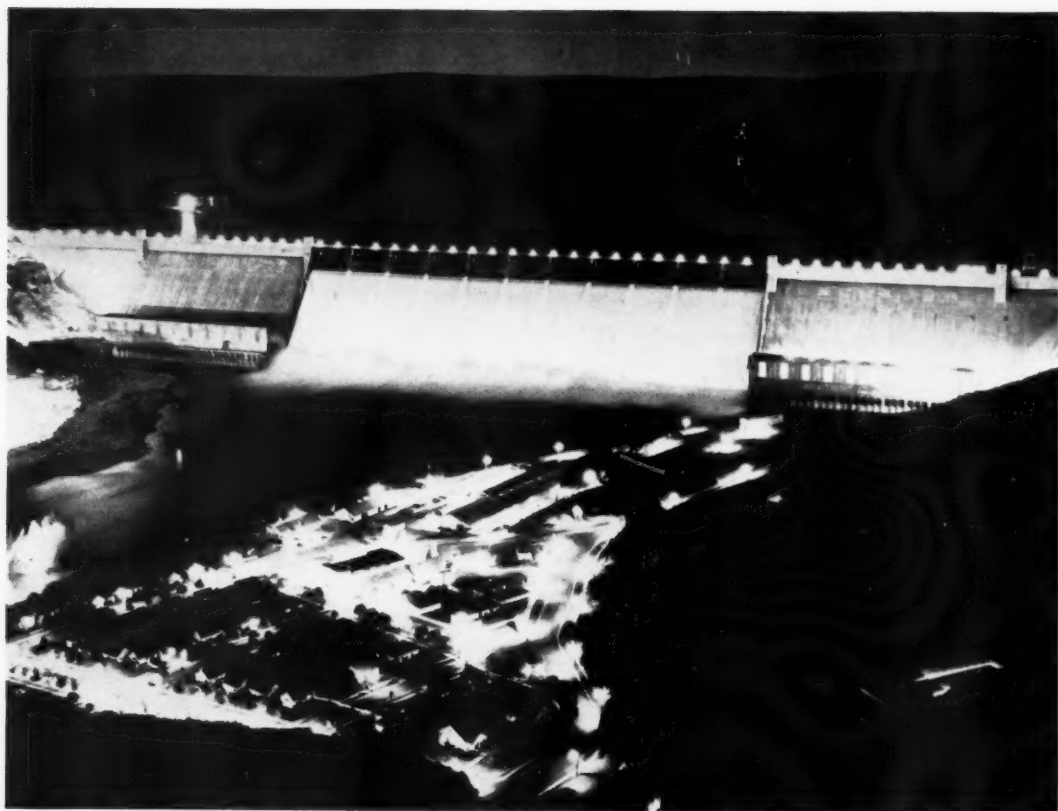


GREASE TESTING BY THE TORQUE-BREAKDOWN MACHINE

- A. An insulated jacket for controlling temperature of test. Test bearing is attached to end of shaft K.
- B. $\frac{1}{4}$ " line leading to inside of jacket. This carries either steam or cold brine.
- C. Potentiometer for obtaining temperature of outer bearing race.
- D & E. Levers for transposing torque forces onto platform of gram scale, F.
- G. 1750 rpm., one hp. induction motor, directly connected to shaft K.
- H. 900 rpm., $\frac{3}{4}$ hp. induction motor which can be geared down to obtain shaft speed of 36 rpm. when necessary.
- I. Clutch lever for driving with either 1750, 900 or 36 rpm. Motor H drives through motor G.
- J. Shaft hangers.
- L. Motor starting switches.



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